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Final Report: Ionization chemistry of high temperature molecular fluids

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Final Report: Ionization chemistry of high temperature molecular fluids

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Objective

With the advent of coupled chemical/hydrodynamic reactive flow models for high explosives, understanding detonation chemistry is of increasing importance to DNT. The accuracy of first principles detonation codes, such as CHEETAH, are dependent on an accurate representation of the species present under detonation conditions. Ionic species and non-molecular phases are not currently included coupled chemistry/hydrodynamic simulations. This LDRD will determine the prevalence of such species during high explosive detonations, by carrying out experimental and computational investigation of common detonation products under extreme conditions.

We are studying the phase diagram of detonation products such as H_2O , or NH_3 and mixtures under conditions of extreme pressure ($P > 1$ GPa) and temperature ($T > 1000\text{K}$). Under these conditions, the neutral molecular form of matter transforms to a phase dominated by ions. The phase boundaries of such a region are unknown.

Technical Approach:

Studying chemistry at extreme conditions ($0.1 \text{ GPa} < P < 200 \text{ GPa}$, $700 \text{ K} < T < 4000 \text{ K}$) is imperative to understanding high explosive detonation processes, as well as the composition of planetary interiors. We propose to examine chemical processes under extreme conditions *in situ* that have so far remained unexplored. Our approach combines three novel elements: first, we have implemented a novel internally heated DAC which can flexibly be combined with laser heating. Second, we have developed unique high-intensity, *in situ* Raman spectroscopic diagnostics. With these diagnostics, we will be able to monitor changes in chemical speciation and sample structure. Third, we are performing terascale simulations of simple fluids and mixtures under extreme conditions, and directly simulating spectroscopic observables from first principles.

Accomplishments

Experiments on the phase diagram of water under extreme conditions have been successfully carried out and published in Physical Review Letters [1]. This work has received significant scientific publicity, including news articles in Nature and Physical Review Focus.

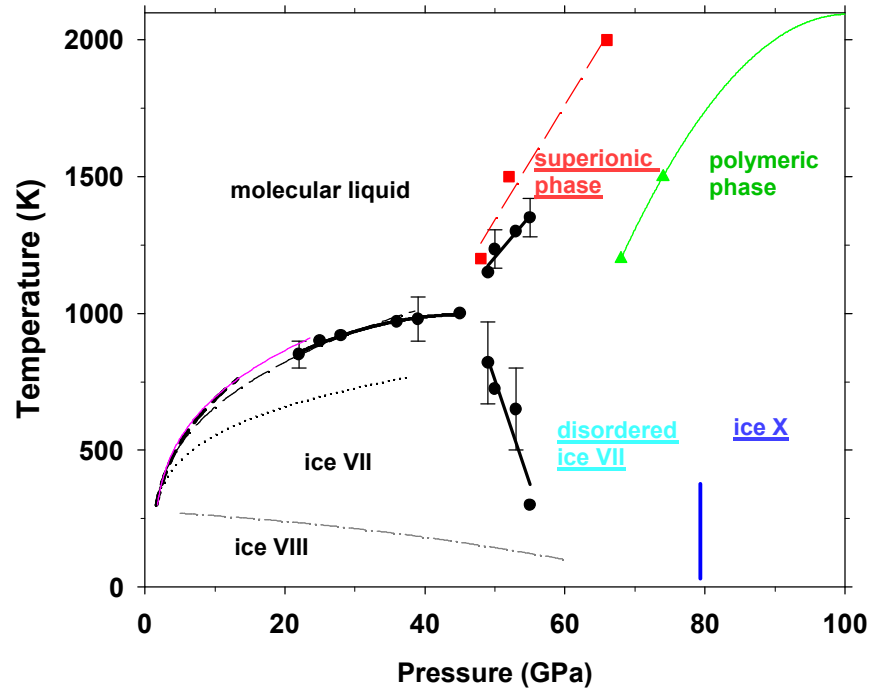


Figure 1: Phase diagram of H₂O. Solid circles correspond to the transformation points determined from our spectral data. The red squares are theoretical calculations of the boundary between the superionic phase and the liquid phase. The green triangles show a second phase transformation, predicted theoretically, to a non-molecular polymeric form of the superionic phase.

We measured Raman spectra of ice and liquid water obtained *in situ* using a laser heated DAC over a wide range of pressure (to 56 GPa) and temperature (to 1500 K) combined with MD simulations under similar conditions. Our most important observation is that there is a sudden change in the slope of the melting curve at 47 GPa and 1000 K. In agreement with these observations, first principles simulations show an apparent transition to a superionic state above 46 GPa. In the superionic state, H atoms are highly mobile while O atoms are fixed. The MD simulations show that water at ca. 40 – 70 GPa and 1000 – 2000 K consists of very short lived H₂O, H₃O⁺ and OH⁻ species (<10 fs), which accounts for the change observed in the O-H stretch intensity that is observed experimentally. The results of this study are summarized in Figure 1, which shows the phase diagram of water determined by our work.

Our results show that superionic phases of water are important at pressures over 47 GPa. This pressure is over the Chapman-Jouget pressure of a common explosive such as HMX (40 GPa). This means that the superionic phase is not likely to be formed during a steady-state detonation. The pressures can be achieved, however, during transient events. Colliding detonation waves, detonations in convergent geometries, or reflected detonation waves are possible examples.

We have also extended our computational studies to higher temperatures than currently achievable experimentally (2000K) and higher pressures (up to 1 Mbar). Our motivation is to accurately determine whether superionic or other non-molecular phases could exist at temperatures typical of a high explosive detonation (2000-3000K). We found a transformation from a molecular form of the superionic phase to a polymeric form demonstrating symmetric hydrogen bonding. The phase boundary is shown in Figure 1.

The results of this study have been accepted in a second Physical Review Letter [2]. Studies have also been performed on formic acid under extreme conditions [3]. An application was also made to the chemical equilibrium of complex fluid mixtures under high P, T conditions [4]. We have showed that symmetric hydrogen bonding may occur across a wide range of molecules [5]. This work generated substantial interest at conferences, including a plenary presentation at the APS Symposium on Shock Compression of Condensed Matter in 2005[6-7].

Exit Strategy

The discoveries generated with this LDRD will be coordinated with Advance Strategic Computing (ASC) efforts in high explosive modeling. Developments in Cheetah (or CHEQ) will take advantage of new knowledge of high-pressure chemistry. The enhancement in the Cheetah and CHEQ models will lead to highly accurate coupled chemistry/hydrodynamic simulations that can treat a wide range of explosive materials. Once the capability is fully established, first principle modeling efforts can take place within the ASC program. Experimental activities can be transitioned to the DoD/DOE Joint Munitions Technology Program, once their relevance to high explosive detonation is established. The PI is active in both of these programs, which will aid in transition.

Publications

- [1] A. Goncharov, N. Goldman, L. Fried, J. Crowhurst, C. Mundy, W. Kuo, J. Zaug, *Phys. Rev. Lett.*, **94**, 125508(2005), UCRL-JRNL-205550.
- [2] N. Goldman, L. Fried, C. Mundy, W. Kuo, *Phys. Rev. Lett.* **94**, 217801, UCRL-JRNL-209577
- [3] A. F. Goncharov, M. R. Manaa, J. M. Zaug, R. H. Gee, L. E. Fried, W. B. Montgomery, "Polymerization of formic acid under high pressure", *Phys. Rev. Lett.*, **94**, 065505(2005), UCRL-JRNL-206204.
- [4] Generation of methane in the Earth's mantle: *In situ* high pressure–temperature measurements of carbonate reduction, H. P. Scott, R. J. Hemley, H. K. Mao, D. R. Herschbach, L. E. Fried, W. M. Howard, and S. Bastea, *Proc. Nat. Acad. Sciences*, US 101: 14023-14026(2004), UCRL-JRNL-206515
- [5] N. Goldman, L. E. Fried, "First principles simulation of a superionic phase of hydrogen fluoride (HF) at high pressures and temperatures", *J. Chem. Phys.*, 125, Art. No. 044501, (2007), UCRL-JRNL-220577.
- [6] L. E. Fried, N. Goldman, I. F. W. Kuo, C. J. Mundy, "Non-molecular phases of H₂O and HF Under Detonation-Like Conditions", 13 Symposium (International) on Detonation, McLean, VA, 2006, UCRL-PROC, 222768
- [7] L. E. Fried, N. Goldman, I. F. W. Kuo, C. J. Mundy, "Chemistry of H₂O and HF Under Extreme Conditions", *Proceedings of the APS Meeting on Shock Compression of Condensed Matter*, Baltimore, MA, 2005, UCRL-CONF-217385.